Results from the Monitoring Network in the Alpine Region for POPs – MONARPOP

POLYBROMINATED DIPHENYL ETHER (PBDE) IN HUMUS LAYERS IN REMOTE FORESTS

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Introduction

Polybrominated diphenyl ether (PBDE) are heavily used as flame retardants in plastics and textiles and have therefore become ubiquitous (de Wit 2002, Letscher & Behnisch 2003). There exist three technical products: Pentabromodiphenylether (PentaBDE) mix, octabromodiphenylether (OctaBDE) mix and decabromodiphenylether (DecaBDE). Because of exponentially increasing levels of the congeners of PentaBDE and OctaBDE mix in human blood and milk (Hites 2004), these two products were banned in many countries (BSEF, EU 2003, NCEL) and industry voluntarily ceased production (Tullo 2003). Decabromodiphenylether was not included in these bans because it is believed to have low bioaccumulation (EU 2004) and low long-range air transport potential (Wania & Dugani 2003). About 8000 t DecaBDE were used in EU countries in 2004 (EBFRIP 2005). Industry tries to reduce existing emissions throughout the live-cycle and sponsors a deca-monitoring programme (BSEF).

Plant surfaces were already used for sampling of PBDE from air. (Hassanin 2005, Mariussen 2005, Ohta 2002, Okazawa 2004, Schlabach & Gjerstad 2006, Schütz 2004, Zhu & Hites 2006). Especially the rough canopy of coniferous forests combs the bypassing air for pollutants and conifer needles efficiently trap lipophilic organic compounds due to their highly absorbing epicuticular wax. The topsoil humus layers in forests with their high organic carbon content accumulate POPs from deposition and fall of needles over a long period (Weiss 2002). For this study humus samples from remote Norway spruce (*Picea abies*) forests were analysed for PBDE.

This paper presents results from the **Mo**nitoring **N**etwork in the **A**lpine **R**egion for **P**ersistent and other **O**rganic **P**ollutants (MONARPOP, Bassan 2005). Its main goal is to investigate the actual contamination of the Alps and to understand the role of high mountains in the global atmospheric transport of POPs (Daly & Wania 2005, Vighi 2006).

Materials and Methods

Humus Sampling

56 humus samples from remote Norway Spruce forest sites in the Alps were sampled for PBDE analysis. This was done by collecting the entire humus layer within a 30 x 30 cm metal frame. Ten pits along a 5 x 30 m rectangular grid were collected systematically and mixed to one sample. This yielded up to 60 l of humus per sampling plot.

Analytical Method

In indoor dust high concentrations of PBDE were detected (Knoth 2003, 2006). Therefore, a clean laboratory environment is essential for the analysis of PBDE, in particular for the analysis of DecaBDE. Polymer material (e.g. red rubber septa) was tested before use. Silica, sodium sulfate and glass wool were extracted with dichloromethane. After evaporation of the solvent, silica and sodium sulfate and all laboratory glassware used for the clean-up procedure were baken out for 16 hours at 450°C. Glass fibre extraction thimbles and filters, Pasteur pipettes and glass wool, which became brittle if heated so long, were immediately cooled down after heating up. After cooling down the glassware was immediately capped with aluminium foil or stored in metal boxes until usage. Sodium hydroxide water solution for the preparation of SiO_2-NaOH was extracted three times with dichloromethane. To avoid cross contamination the vapour tubes of the rotary evaporators were changed after each sample.

20 g freeze-dried and homogenized humus sample was spiked with the $^{13}C_{12}$-BDE standard mixture (1 ng BDE 28, 47, 99; 2 ng BDE 153, 154, 183 and 5 ng BDE 209) and extracted by Soxhlet extraction (Knöfler-Böhm hot extractor). Residual water (0-11%) was simultaneously distillated with Dean-Stark water separator with toluene. The extract was cleaned by a four column clean-up (1. Multi-layer SiO_2-H_2SO_4, NaOH. 2. Macro alumina. 3. GPC bio-beads S-X3. 4. Mini alumina), spiked with the injection standard (1 ng $^{13}C_{12}$-BDE 138) and reduced to 50 µl. 1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC-SIM(EI+)HRMS (TRACE GC-MS MAT 95 XP, ThermoFinnigan, Bremen) using a DB-5MS (15 m x 0.25 mm, 0.1 µm). The two most intense masses of the bromine cluster (Tri- and TeBDE: M^+. Te- to DeBDE: M^+-2Br) were measured for each homologue group. The identification of PBDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the $^{13}C_{12}$-labeled internal standards. All congeners except BDE 100 were quantified based on their corresponding $^{13}C_{12}$-labeled analogues used as internal standards. BDE 100 was quantified using the $^{13}C_{12}$-BDE 99 internal standard. PBDE concentrations were recalculated with conversion factors to reduce freeze-dried to oven dry (at 105°C) humus mass.

All samples were analysed at the German Federal Environment Agency. The laboratory took part in the BSEF/QUASIMEME interlaboratory study on brominated flame retardants December 2001 to March 2002 and the interlab trial for ISO/DIS 22032 November 2004 to February 2005. Method blanks were spiked on a plug of glasswool in a Soxhlet extraction thimble and extracted and clean-up processed every four samples. Blank concentrations were calculated on a fictive mean sample weight of 18.3 g d.m.. The method detection limit (MDL) was determined as the mean concentration in the blank plus 3 times the standard deviation of 19 measurements (Table 1).

Results and Discussion

PBDE were detected in all humus samples. The total concentration of six significant congeners of the technical PentaBDE mix (∑BDE 28+47+99+100+ 153+154) ranges from 190 to 1500 (median 490) and the significant congener of the technical OctaBDE mix (BDE 183) from 14 to 3000 (median 140) ng kg^{-1} d.m.. Although four multimedia models predicted for DecaBDE (BDE 209) a very low potential to reach remote areas (Wania & Dugani 2003) levels from 610 to 85000 (median 1400) ng kg^{-1} d.m. were observed. (Table 1 and Fig. 1-3). A contribution of local but until now unknown sources is probable for two very high BDE 209 concentrations (29000 and 85000 ng kg^{-1} d.m.) (Fig. 3).

The dominating congeners in the humus samples are BDE 209 (51-97%), BDE 183 (0.7-31%), BDE 47 and BDE 153 (both 0.2-18%) and BDE 99 (0.1-13%). The contribution of the other congeners is of minor importance (BDE 100 0.03-3, BDE 154 0.1-1.5 and BDE 28 0.01-0.4%). BDE 183 is a minor congener in many environmental samples. Its higher percental contribution in humus layers may be due to revolatilisation of the congeners with less than seven bromine from humus to air (Fig. 4).

Table 1. Concentrations of PBDE in humus layers in Norway spruce forests in the Alpine region

	concentration [ng kg^{-1} d.m.]								
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	Σ 6 BDE	BDE 183	BDE 209
n	56	56	56	56	56	56	56	56	56
min	2	93	46	12	7	6	191	14	611
max	19	745	463	110	575	71	1472	3037	84504
5%	2	97	52	14	12	6	207	23	674
10%	3	104	56	15	16	7	220	28	823
25%	4	141	70	19	28	10	313	65	1064
50%	5	252	124	35	39	16	485	139	1414
75%	7	320	197	55	74	31	795	297	2550
90%	10	504	326	82	174	49	1028	789	7483
MDL	1	49	16	4	2	1	73	4	133

Σ 6 BDE = BDE 28+47+99+100+153+154

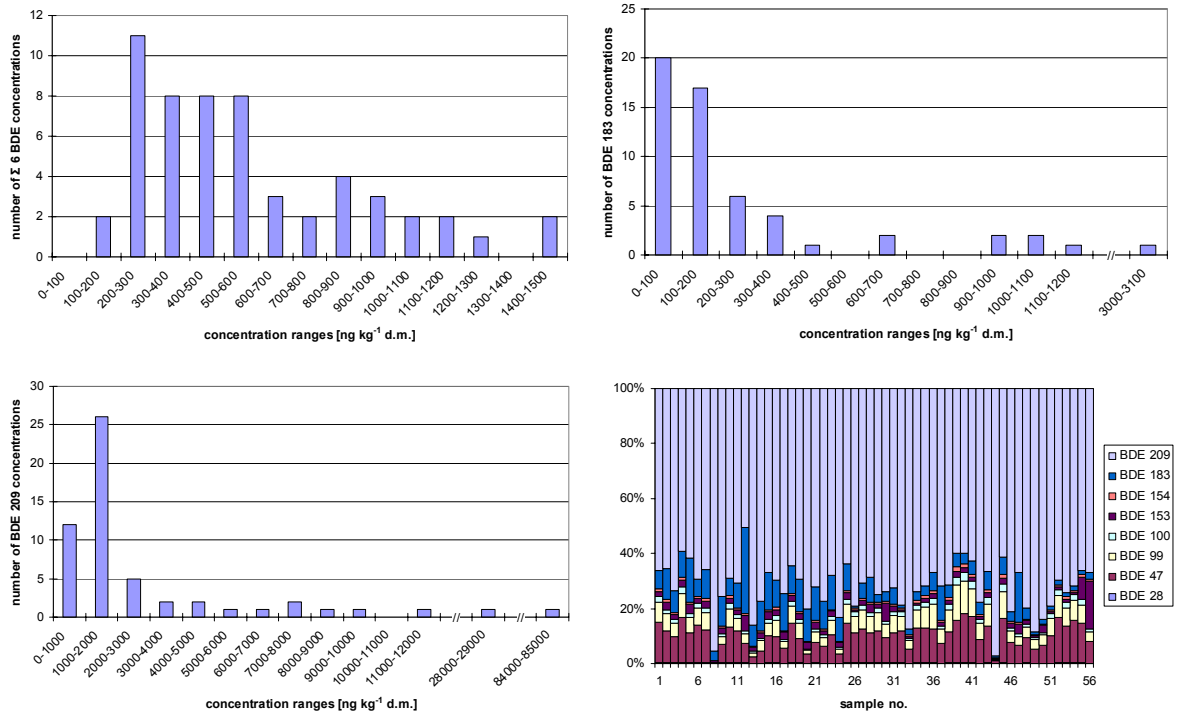

Fig. 1-3. Frequency histogram of Σ 6 BDE (BDE 28+47+99+100+153+154), BDE 183 and BDE 209 concentrations in humus layers in Norway spruce forests in the Alpine region.

Fig. 4. PBDE congener profiles in humus layers in Norway spruce forests in the Alpine region.

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References

Alpine Space. INTERREG III B Alpine Space Programme. <http://www.alpinespace.org/ (January 17, 2007)>

Bassan R, Belis C, Heublein D, Iozza S, Jakl T, Jakobi G, Kirchner M, Knoth W, Kräuchi N, Levy-Lopez W, Luchetta A, Magnani T, Moche W, Oehme M, Offenthaler I, Perthen-Palmisano B, Schmid D, Schramm K-W, Schrott H, Schröder P, Sedivy I, Simoncic P, Uhl M, Weiss P. Monitoring network in the Alpine region for persistent and other organic pollutants: A multinational approach to investigate the contamination of the Alps with organic compounds. *Organohalogen Comp* 2005;67:1839.

BSEF. Bromine Science and Environmental Forum. <http://www.bsef.com/ (January 17, 2007)>

Daly GL, Wania F. Organic contaminants in mountains. *Environ Sci Technol* 2005;39,385.

de Wit CA. An overview of brominated flame retardants in the environment. *Chemosphere* 2002;46:583.

EBFRIP. European brominated flame retardant industry panel. Decabromodiphenyl ether (Deca-BDE) usage in EU countries in 2004 in metric tons. 27 May 2005, 1 p.

EU 2003. Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). *Official Journal of the European Union* 2003;L42:45.

EU 2004. Update of the risk assessment of bis(pentabromophenyl)ether (decabromodiphenyl ether). Final environmental draft of May 2004. CAS No. 1163-19-5, EINECS No. 214-604-9, 114pp.

Hassanin A, Johnston AE, Thomas GO, Jones KC. Time trend of atmospheric PBDEs inferred from archived U.K. herbage. *Environ Sci Technol* 2005;39:2436.

Hites RA. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ Sci Technol* 2004;38:945.

Knoth W, Mann W, Meyer R, Nebhuth J. Brominated diphenyl ether in indoor dust. *Organohalogen Comp* 2003;61:207.

Knoth W, Mann W, Meyer R, Nebhuth J. Humus from coniferous forests a reservoir for PBDE from air and deposition – analysis and quality control. *Organohalogen Comp* 2006;68:1163

Letcher RJ, Behnisch PA, Ed.. The state-of-the science and trend of BFRs in the environment. *Environment international* 2003;29:663.

Mariussen E, Steinnes E, Gundersen H, Borgen A, Schlabach M. Analysis of polybrominated diphenyl ethers in moss (*Hylocomium splendens*) from the Norwegian environment. *Organohalogen Comp* 2005;67:591.

MONARPOP. Monitoring network in the Alpine Region for persistent and other organic pollutants. <http://www.monarpop.at/ (January 17, 2007)>

NCEL. National Caucus of Environmental Legislators. Bulletins March 4 and May 31, 2005. <http://www.ncel.net/base.cgim?template=bulletins_archive (January 17, 2007)>

Ohta S, Ishizuka D, Nishimura H, Nakao T, Aozasa O, Shimidzu Y, Ochiai F, Kida T, Nishi M, Miyata H. Comparison of polybrominated diphenyl ethers in fish, vegetables and meats and levels in human milk of nursing women in Japan. *Chemosphere* 2002;46:689.

Okazawa T, Hanari N, Guruge K, Wzykowska B, Orlikowska A, Yamashita N, Falandysz J. Congener-spezific data of PBDEs in pine needles. *Organohalogen Comp* 2004;66:3725.

Schlabach M, Gjerstad KI. Deposition of airborne BFR around the city of Ålesund, Norway. *Organohalogen Comp* 2006;68:73

Schütz A. Bestimmung polybromierter Diphenylether (PBDE) in Umweltproben unter besonderer Berücksichtigung des DecaBDE. Diplomarbeit, Universität Ulm, Abteilung Analytische Chemie und Umweltchemie 2004;146 pp.

Tullo A. Flame-retardant phase out. *Chemical & Engineering News* November 10, 2003:13.

Vighi M, Ed.. The role of high mountains in the global transport of persistent organic pollutants. *Ecotoxicology and Environmental Safety* 2006;63:1.

Wania F, Dugani CB. Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environ Toxicol Chem* 2003;22:1252.

Weiss P. Organische Schadstoffe an entlegenen Waldstandorten Sloweniens und Kärntens. Berichte BE-195. Umweltbundesamt GmbH, Wien, September 2002. ISBN 3-85457-616-1. 121 S.

Zhu L, Hites RA. Brominated flame retardants in tree bark from North America. *Environ Sci Technol* 2006;40:3711.